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EXPERIMENTS WITH CERTAIN COPPER COMPOUNDS AS BUNT FUNGICIDES

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INTRODUCTION

The effectiveness of copper sulphate and copper carbonate in controlling bunt, or stinking smut, of wheat (*Tilletia tritici* (Bjerk.) Wint. and *T. levis* Kühn) in early experiments soon led to the general observation that copper salts seem to be peculiarly toxic to the spores of this fungus. Since its introduction by Darnell-Smith (*1*)[1] copper carbonate has been the principal copper salt used as a dust fungicide for bunt control, but others at times have been reported effective for this purpose (*4*) and a few have been used to a considerable extent. None, however, has reached the stage of successful commercial production attained by the carbonate. It was thought that some of these other compounds of copper (or possibly of other metals) might be sufficiently effective, cheap, and abundant to compete successfully with copper carbonate as fungicides for the control of bunt. A number of such compounds were therefore obtained or prepared, and after certain laboratory studies some were tested in field experiments on the Arlington Experiment Farm, Rosslyn, Va., during the period from 1930 to 1935.

REVIEW OF LITERATURE

The literature on the early development of bunt fungicides has been reviewed by Woolman and Humphrey (*7*) and by Mackie and Briggs (*2*). The latter carried out extensive experiments on bunt control with copper carbonate and copper sulphate and suggested a set of qualifications for copper carbonate when it is to be used as a bunt fungicide. They found pulverized copper sulphate less satisfactory than copper carbonate as a bunt preventive.

[1] Italic numbers in parentheses refer to Literature Cited, p. 8.

Muncie and Frutchey (*3*) in 3 years' field experiments tried 41 dusts, among which were such copper compounds as the carbonate, sulphate, oxychloride, phosphate, bordeaux powder, and various mixtures of these with other materials. On the whole they found copper carbonate superior to the other copper dusts used.

Twentyman (*6*) obtained satisfactory bunt control with anhydrous and basic copper sulphates, copper acetate, copper oxychloride, and mixtures of certain of these compounds, but he demonstrated that the effectiveness of a dust may be governed largely by its physical properties as well as by its chemical composition.

Petit (*4*) recommended the following compounds of copper for bunt control, either undiluted or at various dilutions according to the spore load on the seed: Chloride, arsenite, nitrate, bromide, fluosilicate, anhydrous sulphate, arsenate, oxychloride, neutral acetate, iodide, oxalate, citrate, and carbonate. Among the copper salts generally found ineffective as bunt fungicides he mentions the following: Sulphophenate, sulphide, sulphocyanide, oxides, phosphate, silicate, cyanide, formate, borate, tartrate, phosphide, chromate, and dichloroacetate. It seems that Petit failed to take into consideration the corrosiveness, hygroscopicity, or other objectionable characteristics of some of the materials he recommended.

Schwaebel (*5*) reduced bunt infection to less than 0.5 percent with basic copper chloride and copper oxychloride, while copper carbonate failed to reduce it to less than 7.5 percent. It is possible that the brand of copper carbonate he used may not have possessed the qualifications suggested by Mackie and Briggs.

Other investigators at times have reported more or less satisfactory results from the use of different copper compounds in experiments on bunt control, but at present these materials, with the possible exception of basic copper sulphate, do not offer any serious competition to copper carbonate on the market.

MATERIALS AND METHODS

COMPOSITION AND APPLICATION OF COMPOUNDS TESTED

In the experiments reported herein copper carbonate containing approximately 50 percent of copper was used as a standard of comparison. Certain commercial brands of copper carbonate containing 18 to 20 percent of copper were also used. This material was used full strength only. Other more or less common compounds of copper tested were as follows: Normal sulphates (dehydrated and monohydrate), basic sulphate, oxychloride, phosphate, silicate, and cupric and cuprous oxides. The phosphate, silicate, and cuprous oxide were used both full strength and diluted with equal weights of bentonite. The acetate, chlorides (cupric and cuprous), nitrate, cyanide, iodide, borate, and many other materials were used only in preliminary laboratory or greenhouse experiments, which revealed in them certain characteristics highly undesirable in dust fungicides. Two noncopper compounds upon which comparative data were available were also included: A proprietary organic mercury compound containing 2 percent of ethyl mercuric chloride in 1933 and 1934 and one containing 5 percent of ethyl mercuric phosphate in 1934 and 1935.

In addition to the above-mentioned compounds the following products were prepared in the laboratory:

N–1, a cuprous sulphide containing 74.7 percent of copper, was prepared by heating sulphur mixed with copper foil. The sample contained some free sulphur or cupric sulphide.

N–2, a copper fluoride-aniline compound containing 9.0 percent of fluorine and 61.9 percent of copper, was prepared by adding aniline to a solution of copper fluoride and heating the mixture to boiling. The reddish-bronze crystals which precipitated were washed several times with water and dried at 110° C.

N–3, a copper fluoride containing 50.8 percent of copper and 24.1 percent of fluorine, was prepared by mixing 1 mole of basic copper carbonate ($CuCO_3.Cu(OH)_2$) with a solution containing 6 moles of hydrofluoric acid in a copper dish. The light-blue precipitate was washed and dried at 110° C. This preparation probably contained some basic copper fluoride.

N–4, a copper fluoride containing 58.6 percent of copper and 16.2 percent of fluorine, was prepared by neutralizing basic copper carbonate with 40-percent hydrofluoric acid in a copper dish.

N–5, a copper fluoride-aniline preparation, was made as follows: Copper fluoride (CuF_2) was prepared by mixing equimolecular quantities of potassium fluoride and copper sulphate ($CuSO_4.5H_2O$). A bluish-white powder precipitated, leaving the solution a greenish blue. To the filtered solution was added an excess of aniline, whence a greenish precipitate was obtained. This precipitate was washed with water and alcohol and dried 24 hours at 110° C. The resulting powder, containing 13.3 percent of copper, was insoluble in water and in a number of common organic solvents.

N–6, a copper sulphate-aniline preparation containing 20.6 percent of copper, was made by adding aniline to a solution of copper sulphate. The precipitate was washed with alcohol and water and dried 24 hours at 110° C.

N–7, a copper diazoaminobenzene compound, was prepared by adding an excess of ammoniacal copper sulphate to diazoaminobenzene dissolved in alcohol. The mixture was refluxed for 3 to 5 hours, whence a blue powder separated out. After the filtered solution had been allowed to cool, a dark bronze-colored powder precipitated, which on analysis gave 20.6 and 17.9 percent of copper, respectively, for two preparations.

N–8 was similar to N–7 except that para-aminobenzene was substituted for diazoaminobenzene. The product appeared as bluish flaky crystals, which were almost transparent under the microscope and contained 41.9 percent of copper.

N–9, a cupric chloride-aniline preparation, was made by adding aniline to a solution of cupric chloride until no more aniline reacted. A dark-brown to black powder containing 19.8 percent of copper was precipitated. Its exact composition was not determined.

Each of these laboratory preparations was used full strength and also diluted with an equal weight of talc and with twice its weight of talc.

These dust fungicides were applied to spore-infested seed of Purplestraw wheat at the rate of 2 ounces per bushel, with the exception of the proprietary compound containing ethyl mercuric phosphate, which was used at the rate of only one-half ounce per bushel. The dust and the seed were thoroughly agitated in a mechanical mixer until the seed was evenly coated.

SEED AND INOCULUM USED

Purplestraw wheat, which is rather susceptible to bunt, was used in these experiments. It was obtained from plots on the Arlington Farm. The bunt was obtained from plots of ripe Purplestraw wheat also grown on the Arlington Farm. The bunt balls were either separated from threshed bunt-infested wheat or obtained from infected heads that had been picked by hand from the ripe harvested bundles. The bunt balls were broken up and put through a series of sieves, the last one being 60-mesh. The spores were kept in a closed container in the laboratory until used.

The bunt spores were applied to the seed at the rate of 1 part of spores by weight to 250 parts of seed in the experiments of 1930–31, and at the rate of 1 to 100 in the experiments of 1931–35. After the inoculum had been applied to the seed, both were thoroughly mixed in a mechanical duster so that the seed was dark with spores.

SOWING THE SEED AND RECORDING THE DATA

The treated and untreated seeds were sown by hand in rod rows in 1930 and 1931, but in 1932, 1933, and 1934 a hand drill was used to insure more nearly uniform sowing. Usually the rate of seeding was 12 to 13 grams per rod row. In the five successive years the numbers of replications were 5, 6, 10, 7, and 6, respectively.

The effect of the different materials on emergence was studied by sowing 300 seeds of each treated lot in the greenhouse along with untreated seed for comparison. Emergence data were taken before the appearance of the second leaf. With few exceptions the dusts improved germination.

Data on bunt occurrence were obtained by counting all the bunted heads in every row and also the total heads in the rows in which more than a trace of bunt appeared. The data on yield were obtained by harvesting each row by hand and threshing it in a small rod-row thresher. The bundles representing the different replications receiving one treatment were grouped together and threshed consecutively to reduce the experimental error.

RESULTS

The data on bunt occurrence and yield obtained in the course of these experiments are summarized in table 1.

TABLE 1.—*Bunt occurrence in, and yields of grain from, Purplestraw wheat grown from bunt-infested seed treated with different dust fungicides and sown in replicated rod rows on the Arlington Experiment Farm, Rosslyn, Va., 1930–35*

Compound	Bunted heads					Yield per acre		
	1930–31	1931–32	1932–33	1933–34	1934–35	1932–33	1933–34	1934–35
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Bushels*	*Bushels*	*Bushels*
Controls (untreated seed), average	47.1	17.7	4.3	90.6	76.9	23.5	9.8	11.6
Copper carbonate:								
High-grade	0	0	.1	.7	.2	28.1	30.3	23.0
18–20 percent Cu	0	0	.2	1.5	.3	24.2	30.4	24.4
Copper sulphate:								
Dehydrated		0	0	.6	.2	27.4	30.4	18.9
Basic		0	0	.5	.2	27.8	31.0	21.2
Monohydrate					.1			21.1
Copper oxychloride		0	0	1.2	.3	24.3	30.6	21.7

TABLE 1.—*Bunt occurrence in, and yields of grain from, Purplestraw wheat grown from bunt-infested seed treated with different dust fungicides and sown in replicated rod rows on the Arlington Experiment Farm, Rosslyn, Va., 1930–35*—Continued

Compound	Bunted heads					Yield per acre		
	1930–31	1931–32	1932–33	1933–34	1934–35	1932–33	1933–34	1934–35
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Bushels*	*Bushels*	*Bushels*
A copper phosphate (44 percent Cu):								
Undiluted		0.2	0.8	1.7	[1] T	30.5	29.6	18.2
Diluted 1–1		.1	T	9.3		25.7	29.9	
A copper silicate (33 percent Cu):								
Undiluted				2.1	.1		26.4	22.9
Diluted 1–1				5.4	2.5		25.6	21.0
Cupric oxide				6.8			27.9	
Cuprous oxide:								
Undiluted					.5			23.0
Diluted 1–1					.4			18.0
Ethyl mercuric chloride, 2 percent			0	.1		24.4	28.8	
Ethyl mercuric phosphate, 5 percent				.3	.3		26.2	23.7
Cuprous sulphide (74.7 percent Cu) (N–1):								
Undiluted	T	.2						
Diluted 1–1	0	.9						
Diluted 1–2		3.0						
Copper fluoride-aniline compound (61.9 percent Cu) (N–2):								
Undiluted	0	0	0	.2	T	25.7	26.0	20.0
Diluted 1–1	0	0	.1	.4	.2	26.7	25.4	20.8
Diluted 1–2		0	.1			27.7		
Copper fluoride (50.8 percent Cu) (N–3):								
Undiluted	0	0	0			26.4		
Diluted 1–1	0	0	.1			29.4		
Diluted 1–2		0	.3			27.9		
Copper fluoride (58.6 percent Cu) (N–4):								
Undiluted	0	0	T	.3	.2	26.3	24.3	18.9
Diluted 1–1	0	0	.2	.5	.1	27.6	27.2	15.7
Diluted 1–2		0	.2			26.2		
Copper fluoride-aniline compound (13.3 percent Cu) (N–5):								
Undiluted	0	0	.1	1.1	.7	26.9	25.5	18.2
Diluted 1–1	0	0	.3	1.8	1.4	28.5	26.5	19.0
Diluted 1–2		0	.9			25.6		
Copper sulphate-aniline compound (N–6):								
Undiluted	0	0	T	1.1	.8	27.6	25.8	19.7
Diluted 1–1	0	.1	.5	3.2	1.1	27.4	29.0	20.7
Diluted 1–2		0	.6			25.2		
Copper diazoaminobenzene compound (N–7):								
Undiluted	0	0	.7			25.4		
Diluted 1–1	0	.1	1.2			25.4		
Diluted 1–2		.2	1.1			24.4		
Copper para-aminobenzene compound (N–8):								
Undiluted		.2						
Diluted 1–1		.4						
Diluted 1–2		1.5						
Cupric chloride-aniline compound (N–9):								
Undiluted			.2	.6	.1	30.5	27.0	20.8
Diluted 1–1			.1	1.6	1.1	27.9	33.5	21.7
Diluted 1–2			.2			26.9		

[1] T = less than 0.1 percent.

EXPERIMENTS IN 1930–31

In 1930–31 all the materials controlled bunt so completely that no comparisons could be made regarding their relative effectiveness. Germination also was improved by most of the dusts, and not impaired by any of them.

EXPERIMENTS IN 1931–32

In the fall of 1931 the seed germinated in a wet soil at a rather high temperature. The conditions were therefore highly unfavorable for bunt infection, as indicated by an average of only 17.7 percent of bunt

in the controls. Infection in the treated lots was reduced to 0.2 percent or less where the dusts were not diluted. Cuprous sulphide and the copper para-aminobenzene compound diluted with talc to one-third their original strength were less effective. In view of the small percentage of infection in the controls, these materials were eliminated on the basis of relative ineffectiveness. These two dusts also reduced slightly the percentage of emerging seedlings; moreover, their relatively high cost renders them impracticable as fungicides.

EXPERIMENTS IN 1932–33

Soil conditions after sowing in the fall of 1932 again were highly unfavorable for bunt development, the average infection in the controls being only 4.3 percent. This light infection was reduced to 0.2 percent or less by all undiluted dusts except copper phosphate and the copper diazoaminobenzene compound, in which cases 0.8 and 0.7 percent of bunt appeared, respectively. The latter dust, when diluted, was the only one to allow more than 1.0 percent of bunt to appear and therefore was eliminated from further tests. Copper fluoride (N–3) also was dropped, as it proved to be highly corrosive to metal because of its fluorine content, and therefore could not be considered as a practical bunt fungicide even if it were effective. Furthermore, its cost would be decidedly more than that of copper carbonate or some of the other more promising fungicides.

All the dusts increased the yield of grain considerably above that from untreated seed, the average increase being 15 percent. The low percentage of bunted heads from untreated seed indicates that the dusts afforded some protection against other diseases.

EXPERIMENTS IN 1933–34

The dusts used during the 1933–34 season were put to a very severe test, as the control rows from untreated seed contained an average of 90.6 percent of bunt. The ethyl mercuric chloride, the copper fluoride-aniline compound (N–2) undiluted, copper fluoride (N–4) undiluted, the ethyl mercuric phosphate preparation, copper fluoride-aniline (N–2) diluted 1–1, copper fluoride (N–4) diluted 1–1, basic copper sulphate, dehydrated normal copper sulphate, cupric chloride-aniline undiluted, and pure copper carbonate were the most effective, in the order named, and reduced infection to less than 1 percent. The other materials reducing infection to less than 2 percent were, in the order of their relative effectiveness, copper fluoride-aniline (N–5) undiluted, copper sulphate-aniline undiluted, copper oxychloride, low-grade copper carbonate, copper chloride-aniline diluted 1–1, copper phosphate undiluted, and copper fluoride-aniline (N–5) diluted 1–1. Copper silicate, copper sulphate-aniline diluted 1–1, diluted copper silicate, cupric oxide, and diluted copper phosphate proved to be slightly less effective.

The average yield from untreated seed was approximately only one-third that from treated seed. Seed treated with cupric chloride-aniline diluted 1–1 gave the highest yield, while that treated with copper fluoride (N–4) undiluted gave the lowest yield of any of the treated lots.

EXPERIMENTS IN 1934–35

Infection was again heavy (76.9 percent) during the 1934–35 season, but bunt control, on the whole, was satisfactory even with some ma-

terials that had failed to reduce infection to less than 2 percent the previous year. None of the materials eliminated bunt entirely, but the only dusts allowing more than 1 percent of infected heads were the diluted forms of copper silicate, copper fluoride-aniline (N–5), copper sulphate-aniline, and cupric chloride-aniline.

The average yield of grain from untreated seed (11.6 bushels per acre) was 40.8 percent less than the average yield from treated seed (19.6 bushels). Seed treated with low-grade copper carbonate yielded best, while that treated with copper fluoride (N–4) diluted 1–1 gave the lowest yield of any of the treated seed.

DISCUSSION

To evaluate the materials tested for use as bunt fungicides, the qualifications of an ideal dust fungicide must be borne in mind. Such a fungicide should be fairly effective in disease control under all conditions without decreasing germination, stand, or yield. It should not endanger the health of operators, and it should be noncorrosive and nonabrasive to the metallic parts of treaters and drills. It should be chemically and physically stable and relatively cheap and abundant. While some fungicides more nearly fulfill these requirements than do others, none is without one or more objectionable features.

Excellent control of bunt was obtained with a number of the compounds used, even when 90.6-percent infection occurred in the controls. Fairly satisfactory control was obtained with all the undiluted dusts used during the last three seasons, with the exception of copper silicate and cupric oxide. The differences in yield from seed treated with the various materials were not highly significant and may be attributed largely to soil heterogeneity and experimental error.

The experimental dusts cuprous sulphide, copper fluoride, copper diazoaminobenzene, and copper para-aminobenzene were discarded for reasons already mentioned. Copper fluoride-aniline (N–2) and copper fluoride (N–4), while fairly effective in bunt control, must be eliminated on the basis of their relative cost, and of their corrosiveness to metal. Copper fluoride-aniline (N–5) would cost more than copper carbonate and is less effective probably because of its relative insolubility.

Copper sulphate-aniline, while slightly less effective than copper carbonate, would be less expensive and fulfills all the other requirements of an ideal dust fungicide as well as does copper carbonate.

Cupric chloride-aniline proved equal to copper carbonate in bunt control but would cost slightly more than the carbonate.

Copper oxychloride, in addition to being somewhat corrosive to metal, is slightly inferior to copper carbonate in fungicidal effectiveness. The phosphate and silicate were not consistently effective in bunt control. Dehydrated copper sulphate and copper sulphate monohydrate, while effective when finely powdered, sooner or later absorb moisture from the air and become lumpy. Cupric oxide is inferior to copper carbonate; and cuprous oxide, although controlling bunt satisfactorily, is more abrasive.

Basic copper sulphate, in addition to being somewhat cheaper than copper carbonate, seems equal, or even superior, to it in fungicidal effectiveness and may be substituted for the carbonate as a bunt fungicide.

SUMMARY

Laboratory, greenhouse, and field studies with a number of copper compounds were carried on over a period of 5 years to determine their relative effectiveness in controlling bunt, or stinking smut, of wheat. Basic copper sulphate, high-grade copper carbonate, copper sulphate-aniline, and possibly copper chloride-aniline, in general, were found to be superior to other copper compounds from the standpoint of cost, general effectiveness in bunt control, and freedom from certain objectionable characteristics. A proprietary dust fungicide containing 5 percent of ethyl mercuric phosphate as its active ingredient was found equal to any of the copper dusts.

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